

## CHAPTER 2

### QUANTUM CHEMICAL METHODS

The quantum chemical methods are divided into 2 classes. The first class comprises of *semiempirical* methods in which a set of empirical parameters are employed, thereby replacing the time-consuming parts of the calculations. The second class of method is *ab initio* which means energies and other properties are calculated from the first principles. For *ab initio* method is summarized in Fig. 2.1.

#### 2.1 The Schrödinger equation

The main target of *ab initio* calculation is to compute energy and other properties of molecule. In quantum mechanics [41], these properties can be gained by solving the solution of the Schrödinger equation,

$$H\Psi = E\Psi \quad (2.1)$$

Here H is the Hamiltonian, a differential operator representing the total energy, which is the sum of kinetic and potential parts,

$$H = T + V \quad (2.2)$$

The first part is the kinetic energy operator T, which is a sum of differential operators,

$$T = -\frac{\hbar^2}{8\pi^2} \sum_i \frac{1}{m_i} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \quad (2.3)$$

The sum is over all particles  $i$  (nuclei and electrons) and  $m_i$  is the mass of particles  $i$ .  $\hbar$  is Planck's constant. The second part is potential energy operator, is the coulomb interaction,

$$V = \sum_{i < j} \left( \frac{e_i e_j}{r_{ij}} \right) \quad (2.4)$$

where the sum is over pairs of particles ( $i, j$ ) with electric charges  $e_i, e_j$  separated by a distance  $r_{ij}$ . For electrons,  $e_i = -e$ , while for a nucleus with atomic number  $Z_i$ ,  $e_i = +Z_i e$ .

$E$  is numerical value of the energy of the state; that is the energy relative to a state in which the constituent particles (nuclei and electrons) are at infinite separation and at rest.  $\Psi$  is the wave function. It depends on the cartesian coordinates of all particles and also on the spin angular momentum components in a particular direction. The square of the wave function,  $\Psi^2$  is interpreted as a measurement of the probability distribution of the particles within the molecule.

The acceptable solutions of eq. (2.1) must be suitable symmetry under interchange of identical particles. For boson particles, the wavefunction is unchanged; that is *symmetric*, under such interchange. For fermion particles, the wavefunction must be multiplied by  $-1$ ; that is *antisymmetric*. Electrons are fermions, so that  $\Psi$  must be antisymmetric with respect to interchange of the coordinates of any pair of electrons. This is termed *antisymmetric principle*.

The Schrödinger equation for any molecules have many possible solutions, corresponding to different stationary states. The state with lowest energy is the ground state.

In molecular system, the Hamiltonian for  $N$  electrons and  $M$  nuclei is

$$\begin{aligned}
 H = & - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \\
 & + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}
 \end{aligned}$$

(in a.u.) (2.5)

In the above equation,  $M_A$  is the ratio of mass of nucleus A to the mass of an electron, and  $Z_A$  is the atomic number of nucleus A. The Laplacian operators  $\nabla_i^2$  and  $\nabla_A^2$  involve differentiation with respect to the coordinates of the  $i$ th electron and  $A$ th nucleus.  $r_{iA}$  is the distance between the  $i$ th electron and  $A$ th nucleus.  $R_{AB}$  is the distance between the  $A$ th nucleus and the  $B$ th nucleus.

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# Ab initio Method

Schrödinger equation

$$H\Psi = E\Psi$$

Slater determinant

$$\Psi(x_1, x_2, \dots, x_N) = (N!)^{-1/2} \begin{vmatrix} \chi_1(x_1) & \chi_j(x_1) & \dots & \chi_k(x_1) \\ \chi_1(x_2) & \chi_j(x_2) & \dots & \chi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(x_N) & \chi_j(x_N) & \dots & \chi_k(x_N) \end{vmatrix}$$

Born-Oppenheimer approximation

$$H_{\text{elec}} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

$$H_{\text{elec}} \Psi_{\text{elec}} = E_{\text{elec}} \Psi_{\text{elec}}$$

Hartree Fock approximation

$$f(i) \chi(x_i) = \epsilon \chi(x_i)$$

Roothaan-Hall equation

$$FC = SC\epsilon$$

SCF Procedure

$$\text{Energy}$$

Figure 2.1 Summary of ab initio method

## 2.2 Molecular orbital theory

Molecular orbital theory is an approach to molecular quantum mechanics, using one-electron functions or orbitals to approximate the full wavefunction. The first major step in simplifying the general molecular quantum mechanics is the separation of the nuclear and electronic motions. This is possible because the nuclear masses are much greater than those of the electrons therefore, nuclei move much more slowly. The separation of the problem into two parts is called the adiabatic or *Born-Oppenheimer approximation* [42]. Therefore, the second term of eq. (2.5), the kinetic energy of the nuclei, can be neglected and the last term of eq. (2.5), the repulsion between the nuclei, can be considered to be constant. The remaining term in eq. (2.5), are called the electronic Hamiltonian ( $H_{\text{elec}}$ ) or Hamiltonian describing the motion of  $N$  electrons in the field of  $M$  point charges,

$$H_{\text{elec}} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (2.6)$$

The corresponding approximation to the total wavefunction is the multiplication product of electronic wavefunction  $\psi_{\text{elec}}(\{\mathbf{r}_i\}; \{\mathbf{R}_A\})$ , which describes the motion of the electrons that explicitly depends on the electronic coordinates, but parametrically depends on the nuclear coordinates and of nuclei wavefunction  $\psi_{\text{nuc}}(\{\mathbf{R}_A\})$  which describes the vibration, rotation, and translation of a molecule.

$$\Psi(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) = \psi_{\text{elec}}(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) \psi_{\text{nuc}}(\{\mathbf{R}_A\}) \quad (2.7)$$

The solution to a Schrödinger equation involving the electronic Hamiltonian,

$$H_{\text{elec}} \psi_{\text{elec}} = \epsilon_{\text{elec}} \psi_{\text{elec}} \quad (2.8)$$

The electronic energy,  $\epsilon_{\text{elec}}$ , is also parametric on the nuclear coordinates,

$$\epsilon_{\text{elec}} = \epsilon_{\text{elec}}(\{R_A\}) \quad (2.9)$$

The total energy for fixed nuclei must also include the constant nuclear repulsion energy,

$$\epsilon_{\text{tot}} = \epsilon_{\text{elec}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.10)$$

The nuclear Hamiltonian ( $H_{\text{nuc}}$ ) for the motion of the nuclei in the average field of the electrons,

$$\begin{aligned} H_{\text{nuc}} &= - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \left\langle - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right\rangle \\ &\quad + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \\ &= - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \epsilon_{\text{elec}}(\{R_A\}) + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \\ &= - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \epsilon_{\text{tot}}(\{R_A\}) \end{aligned} \quad (2.11)$$

The total energy  $\epsilon_{\text{tot}}(\{R_A\})$  provides a potential for nuclear motion. This function constitutes a potential energy surface.

The electronic Hamiltonian in eq. (2.6) depends only on spatial coordinates of the electrons. To describe the behavior of an electron, it is necessary to specify its spin. In the context of nonrelativistic theory, there are

two spin function  $\alpha(\omega)$  and  $\beta(\omega)$ , corresponding to *spin up* and *spin down*, respectively. From each spatial orbital,  $\psi(r)$ , one can form two different spin orbitals,  $\chi(x)$

$$\chi(x) = \begin{cases} \psi(r)\alpha(\omega) \\ \text{or} \\ \psi(r)\beta(\omega) \end{cases} \quad (2.12)$$

The four coordinates of electron is denoted by  $x$ ,

$$x = \{r, \omega\} \quad (2.13)$$

The wavefunction for an N-electron system is then a function of  $x_1, x_2, \dots, x_N$ . That is  $\psi(x_1, x_2, \dots, x_N)$ . Wavefunction must corresponds to the antisymmetric or Pauli exclusion principle, a many electron wavefunction must be antisymmetric with respect to the interchange of the coordinates  $x$  (both space and spin) of any two electrons, i.e.,

$$\psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\psi(x_1, \dots, x_j, \dots, x_i, \dots, x_N) \quad (2.14)$$

So the electronic wavefunction must be written as Slater determinant of spin orbital,

$$\Psi(x_1, x_2, \dots, x_N) = (N!)^{-1/2} \begin{vmatrix} \chi_1(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_1(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \quad (2.15)$$

or short notation,

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \left| \chi_i(x_1) \chi_j(x_2) \dots \chi_k(x_N) \right> \quad (2.16)$$

where the factor  $(N!)^{-1/2}$  is a normalization factor.

### 2.3 The Hartree-Fock approximation

The simplest antisymmetric wavefunction, which can be used to describe the ground state of an N-electron system,  $\Psi_0$ , is a single Slater determinant,

$$\Psi_0 = \left| \chi_1 \chi_2 \dots \chi_a \chi_b \dots \chi_N \right> \quad (2.17)$$

The variation principle states that the best wavefunction of this functional form is the one which gives the lowest possible energy,

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \quad (2.18)$$

where H is the full electronic Hamiltonian. The variational flexibility in the wavefunction (2.17) is in the choice of spin orbitals, one can derive eigenvalue equation, called the *Hartree-Fock equation* which determines the optimal spin orbitals of the form

$$f(i)\chi(x_i) = \epsilon\chi(x_i) \quad (2.19)$$

where  $f(i)$  is an effective one-electron operator, called the *Fock operator*, of the form

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{\text{HF}}(i) \quad (2.20)$$



where  $v^{\text{HF}}(i)$  is the average potential experienced by the  $i$ th electron due to the presence of the other electrons. The essence of the Hartree-Fock approximation is to replace the complicated many-electron problem by one-electron problem in which electron-electron repulsion is treated in an average way.

The Hartree-Fock potential  $v^{\text{HF}}(i)$ , or equivalently the “field” seen by the  $i$ th electron, depends on the spin orbitals of the other electrons. Thus the Hartree-Fock equation (2.19) is nonlinear and must be solved iteratively. The procedure for solving the Hartree-Fock equation is called the *self-consistent-field* (SCF) method.

From eq. (2.20), the best (Hartree-Fock) spin orbitals is the Hartree-Fock integro-differential equation

$$h(1)\chi_a(1) + \sum_{b \neq a}^N \left[ \int dx_2 |\chi_b(2)|^2 r_{12}^{-1} \right] \chi_a(1) - \sum_{b \neq a}^N \left[ \int dx_2 \chi_b^*(2) \chi_a(2) r_{12}^{-1} \right] \chi_b(1) = \epsilon_a \chi_a(1)$$

$$\left[ h(1) + \sum_{b \neq a}^N J_b(1) - \sum_{b \neq a}^N K_b(1) \right] \chi_a(1) = \epsilon_a \chi_a(1) \quad (2.21)$$

where  $h(1)$  is core-Hamiltonian operator

$$h(1) = -\frac{1}{2} \nabla_1^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}} \quad (2.22)$$

$J_b(1)$  is the coulomb operator

$$J_b(1) = \int dx_2 |\chi_b(2)|^2 r_{12}^{-1} \quad (2.23)$$

$K_b(1)$  is the exchange operator

$$K_b(1) = \int dx_2 \chi_b^*(2) r_{12}^{-1} P_{12} \chi_b(2) \quad (2.24)$$

Therefore, the Fock operator  $f(1)$  can be written as

$$f(1) = h(1) + \sum_{b=1}^N [J_b(1) - K_b(1)] \quad (2.25)$$

and the Hartree-Fock potential  $v^{\text{HF}}(1)$ ,

$$v^{\text{HF}}(1) = \sum_{b=1}^N [J_b(1) - K_b(1)] \quad (2.26)$$

the orbital energy  $\epsilon_a$ ,

$$\epsilon_a = [a|h|a] + \sum_{b=1}^N [aa|bb] - [ab|ba] \quad (2.27)$$

and 
$$E_0 = \sum_{a=1}^N [a|h|a] + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [aa|bb] - [ab|ba] \quad (2.28)$$

$$E_0 = \sum_{a=1}^N \epsilon_a - \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [aa|bb] - [ab|ba] \quad (2.29)$$

For closed-shell restricted Hartree-Fock wavefunction

$$\begin{aligned} |\Psi_0\rangle &= |\chi_1 \chi_2 \chi_3 \chi_4 \dots \chi_{N-1} \chi_N\rangle \\ &= |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_{N/2} \bar{\psi}_{N/2}\rangle \end{aligned}$$

$$\begin{aligned}
 E_0 &= 2 \sum_{a=1}^{N/2} (\psi_a | h | \psi_a) + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} 2 (\psi_a \psi_a | \psi_b \psi_b) - (\psi_a \psi_b | \psi_b \psi_a) \\
 \text{Thus} &= 2 \sum_{a=1}^{N/2} (a | h | a) + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} 2 (aa | bb) - (ab | ba) \quad (2.30) \\
 &= 2 \sum_{a=1}^{N/2} h_{aa} + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} (2J_{ab} - K_{ab})
 \end{aligned}$$

In eq. (2.30) is the eliminated spin form, the calculation of molecular orbitals become equivalent to the problem of solving the spatial integro-differential equation

$$f(r_i) \psi_i(r_i) = \epsilon_i \psi_i(r_i) \quad (2.31)$$

Solving this equation numerically, Roothaan introduces a set of known *basis functions*  $\{\phi_\mu(r) / \mu = 1, 2, \dots, K\}$  and expand the unknown molecular orbitals in the linear expansion of these functions,

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_\mu \quad i = 1, 2, \dots, K \quad (2.32)$$

The quality of the molecular orbitals is related to the quality of the basis set, set of basis functions, used. The early STO basis function (Slater Type Orbital) introduced by Slater [43], is based on approximation of hydrogen-like atomic orbitals according to empirical rules. They were mostly used for the calculations of small molecules. The advantage of using a few functions of STO gives more accurate representation of atomic orbitals, the integrations of the functions are very time-consuming. The STO form is

$$\phi^{\text{STO}} = N r^{n-1} \exp(-\beta r) Y_{l,m}(\theta, \Phi) \quad (2.33)$$

where  $\beta$ ,  $n$  and  $Y_{l,m}$  are the exponent coefficient, principle quantum number, and the angular part of the wavefunction, respectively.

An alternative to the STOs is the use of a GTO (Gaussian Type Orbital) [44], which represents a STO sum of gaussian functions of the form

$$\phi^{\text{GTO}} = \alpha_i \text{Nexp}(-\beta_i r^2) Y_{l,m}(\theta, \Phi) \quad (2.34)$$

where  $\alpha$  and  $\beta$  are the suitable coefficients and exponents, respectively.

According to the assumption above, the larger the expansion of GTOs, the more equivalence to a STO is obtained. Another type of atomic orbital is the GLO (Gaussian Lobe Orbital) [45],[46] which is the simplest form of basis functions. Its form is

$$\phi^{\text{GLO}} = \text{Nexp}(-\beta r^2) \quad (2.35)$$

The angular part is omitted. Instead, GLOs are combined together to reproduce the conventional orbital shapes.

From eq. (2.31), the problem of calculating the Hartree-Fock molecular orbitals reduces to the problem of calculating the set of expansion coefficients  $C_{\mu i}$ .

By substitution the linear expansion (2.32) into the Hartree-Fock equation (2.31) and using the index  $\nu$ , gives

$$f(1) \sum_{\nu=1}^K C_{\nu i} \phi_{\nu}(1) = \epsilon_i \sum_{\nu=1}^K C_{\nu i} \phi_{\nu}(1) \quad (2.36)$$

then multiply by  $\phi_{\mu}^*(1)$  on the left and integrate

$$\sum_{\nu=1}^K C_{\nu i} \int d\mathbf{r}_1 \phi_{\mu}^*(1) f(1) \phi_{\nu}(1) = \epsilon_i \sum_{\nu=1}^K C_{\nu i} \int d\mathbf{r}_1 \phi_{\mu}^*(1) \phi_{\nu}(1) \quad (2.37)$$

and define two matrices, the overlap matrix  $S$ , has elements

$$S_{\mu\nu} = \int dr_1 \phi_\mu^*(1) \phi_\nu(1) \quad (2.38)$$

and the Fock matrix  $F$ , has elements

$$F_{\mu\nu} = \int dr_1 \phi_\mu^*(1) f(1) \phi_\nu(1) \quad (2.39)$$

Therefore, the integrated Hartree-Fock equation is written as

$$\sum_{\nu=1}^K F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu=1}^K S_{\mu\nu} C_{\nu i} \quad i = 1, 2, \dots, K \quad (2.40)$$

These are the *Roothaan-Hall equations*, proposed by Roothaan [47] and by Hall [48] which can be written as the single matrix equation

$$FC = SC\varepsilon \quad (2.41)$$

where  $C$  is a  $K \times K$  square matrix of the expansion coefficients  $c_{\mu i}$

$$C = \begin{bmatrix} c_{11} & c_{12} & \cdots & c_{1K} \\ c_{21} & c_{22} & \cdots & c_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ c_{K1} & c_{K2} & \cdots & c_{KK} \end{bmatrix} \quad (2.42)$$

and  $\varepsilon$  is a diagonal matrix of the orbital energies  $\varepsilon_i$ ,

$$\epsilon = \begin{bmatrix} \epsilon_1 & & & \mathbf{0} \\ & \epsilon_2 & & \\ & & \ddots & \\ \mathbf{0} & & & \epsilon_K \end{bmatrix} \quad (2.43)$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu} \quad (2.44)$$

where  $H_{\mu\nu}^{\text{core}}$  is the core-Hamiltonian matrix

$$H_{\mu\nu}^{\text{core}} = \int dr_1 \phi_\mu^*(1) h(1) \phi_\nu(1) \quad (2.45)$$

$G_{\mu\nu}$  is the two-electron part of the Fock matrix

$$G_{\mu\nu} = \sum_{\lambda=1}^{N/2} \sum_{\sigma=1}^{N/2} P_{\lambda\sigma} \left[ (\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu) \right] \quad (2.46)$$

$P_{\lambda\sigma}$  is the density matrix

$$P_{\lambda\sigma} = 2 \sum_{a=1}^{N/2} c_{\lambda a} c_{\sigma a}^* \quad (2.47)$$

and  $(\mu\nu|\lambda\sigma) = \int dr_1 dr_2 \phi_\mu^*(1) \phi_\nu(1) r_{12}^{-1} \phi_\lambda^*(2) \phi_\sigma(2) \quad (2.48)$

For solving the Roothaan-Hall equation, iterative process called *Self Consistent Field* (SCF) procedure are required. The outline of mathematical steps to solve the Roothaan-Hall equations for a closed-shell system are shown in Fig. 2.2. More detailed descriptions can be read in the literature [49].

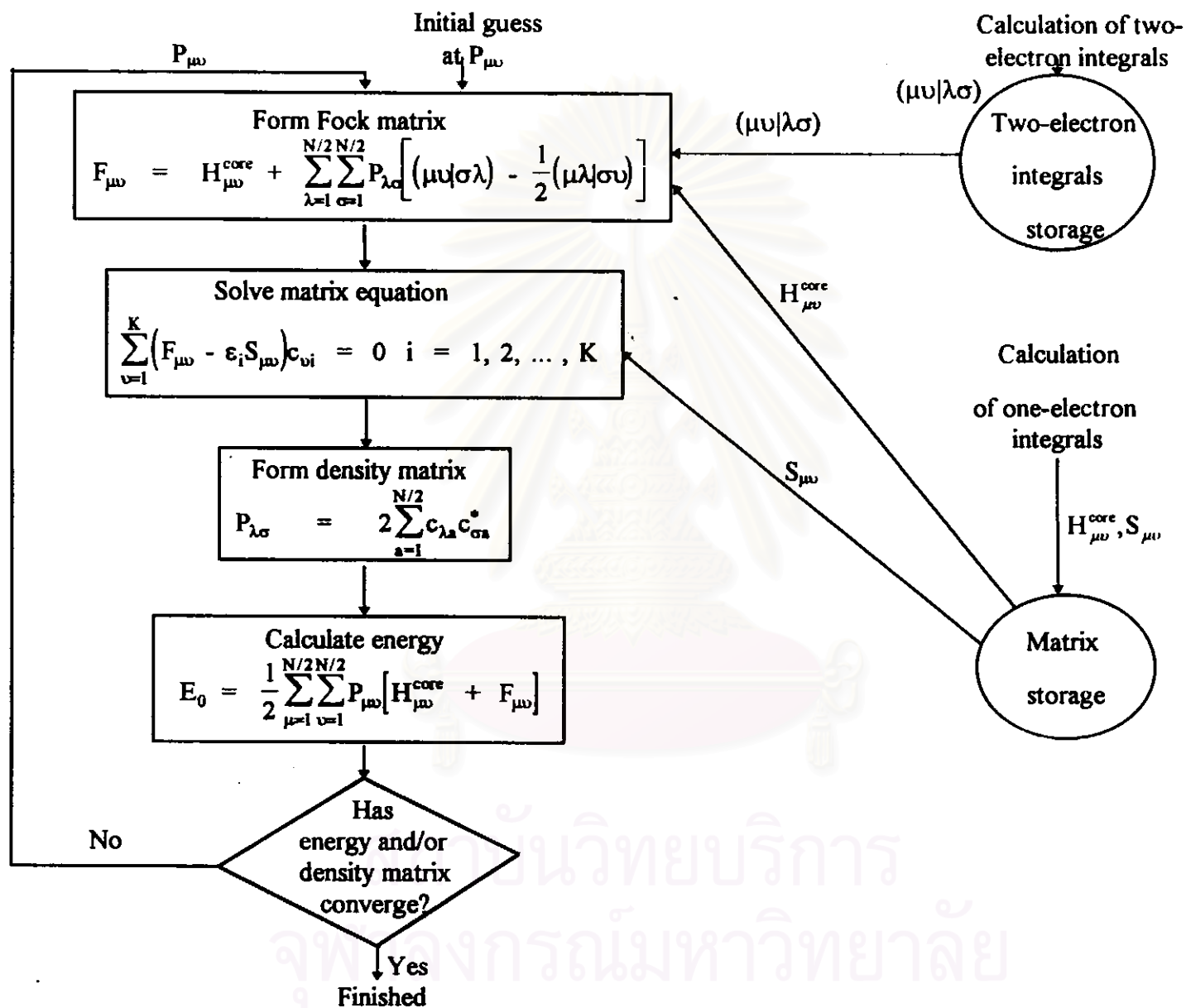


Figure 2.2 The SCF procedure.

## 2.4 Population analysis

The probability of finding an electron in various regions of space,  $\rho(\mathbf{r})$ , is called the charge density and defined as,

$$\rho(\mathbf{r}) = \sum_{\mu=1}^{N/2} \sum_{\nu=1}^{N/2} P_{\mu\nu} \phi_{\mu}(\mathbf{r}) \phi_{\nu}^*(\mathbf{r}) \quad (2.49)$$

Therefore, the total number of electrons is

$$N = 2 \sum_{a=1}^{N/2} \int d\mathbf{r} |\psi_a(\mathbf{r})|^2 \quad (2.50)$$

By substitution eq. (2.32) into eq. (2.50) and using the index  $\mu$ , the eq. (2.50) becomes

$$N = \sum_{\mu=1}^{N/2} \sum_{\nu=1}^{N/2} P_{\mu\nu} S_{\nu\mu} = \sum_{\mu=1}^{N/2} (\mathbf{PS})_{\mu\mu} = \text{trPS} \quad (2.51)$$

$(\mathbf{PS})_{\mu\mu}$  indicated the number of electrons to be associated with  $\phi_{\mu}$ . This is called a *Mulliken population analysis* [50]. The net charge of an atom is given by

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu} \quad (2.52)$$

where  $Z_A$  is the charge of atomic nucleus A.

One important property of molecule involving the electrons distribution is dipole moment,  $\mu$ . The dipole moment of molecule can be calculated as



$$\mu = \left\langle \Psi_0 \left| -\sum_{i=1}^N \mathbf{r}_i \right| \Psi_0 \right\rangle + \sum_A Z_A \mathbf{R}_A \quad (2.53)$$

where the first term is the contribution of the electrons, of charge -1, and the second term is the contribution of the nuclei, of charge  $Z_A$  to the dipole moment. The electronic dipole moment operator is  $-\sum_{i=1}^N \mathbf{r}_i$ , a sum of one-electron operators.

Therefore,

$$\mu = -\sum_{\lambda=1}^{N/2} \sum_{\sigma=1}^{N/2} P_{\lambda\sigma}(\lambda|\mathbf{r}|\sigma) + \sum_A Z_A \mathbf{R}_A \quad (2.54)$$

A vector equation with components (for example the x component) is

$$\mu_x = -\sum_{\lambda=1}^{N/2} \sum_{\sigma=1}^{N/2} P_{\lambda\sigma}(\lambda|x|\sigma) + \sum_A Z_A X_A \quad (2.55)$$

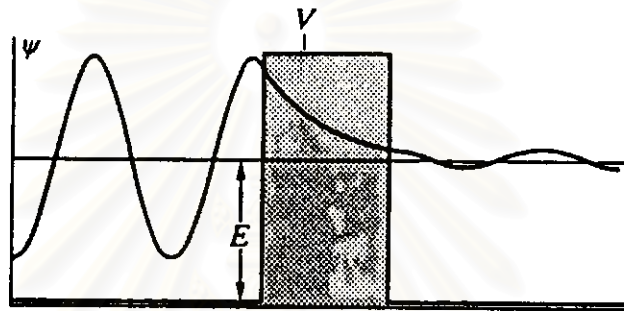
where

$$(\lambda|x|\sigma) = \int d\mathbf{r}_1 \phi_\lambda^*(\mathbf{r}_1) x_1 \phi_\sigma(\mathbf{r}_1) \quad (2.56)$$

With the same manner,  $\mu_y$  and  $\mu_z$  can be also computed.

## 2.5 The tunneling phenomenon

When the particle penetrates with kinetic energy  $E$  through the wall, the wavefunction decays exponentially. If the walls are thin and energy of the particle is less than that of the wall, the decay of the wavefunction ceases, and it begins to oscillate again (Fig. 2.3). Such leakage through classically forbidden zones is named *tunneling* or *barrier penetration*.



**Figure 2.3** A particle with the kinetic energy  $E$  incident on a finite barrier  $V$  (for  $E < V$ ).

Through the Schrödinger equation, the probability of tunneling can be evaluated. The optimal form of the Schrödinger equation is inside a barrier (a region where  $V > 0$ ).

$$\frac{d^2\psi}{dx^2} = \frac{2m(V-E)\psi}{\hbar^2} \quad (2.57)$$

and the general solution of this equation is

$$\psi = Ae^{\alpha x} + Be^{-\alpha x} \quad \text{where} \quad \alpha = \left\{ \frac{2m(V-E)}{\hbar^2} \right\}^{1/2} \quad (2.58)$$

where  $m$  denotes mass of the particle.

To keep the wavefunction finite, the parameter  $A$  is set to zero. Hence the wavefunction inside a long barrier becomes

$$\psi = Be^{-\alpha x} \quad (2.59)$$

that decreases exponentially towards zero as  $x$  increases.

For the finitely long barrier of Fig. 2.4,  $\psi(x)$  is sinusoidal (with amplitude  $A_{in}$ ) inside the wall ( $x < x_0$ ), and decays exponentially within the barrier ( $x_0 < x < x_1$ ). At  $x=x_1$  oscillating starts again with amplitude  $A_{out}$ . The probability of finding the particle inside and outside the wall, beyond the barrier, are proportional to  $A_{in}^2$  and  $A_{out}^2$ , respectively.

Thus the penetration probability,  $P$ , can be written as:

$$P = \left( \frac{A_{out}}{A_{in}} \right)^2 \quad (2.60)$$

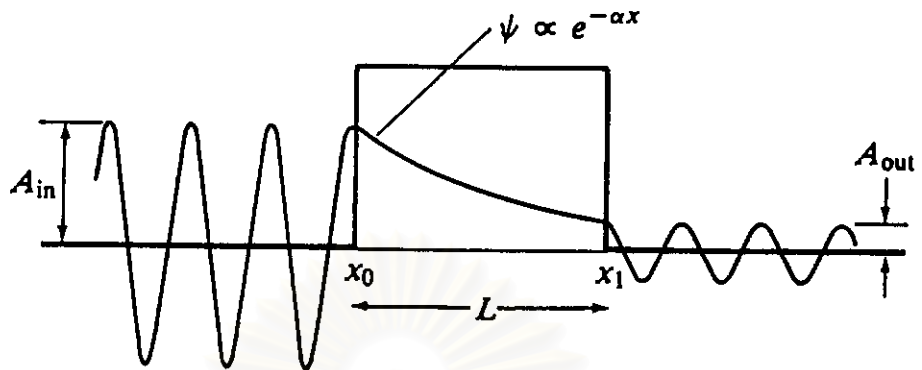
where

$$\frac{A_{out}}{A_{in}} = \frac{e^{-\alpha x_1}}{e^{-\alpha x_0}} = e^{-\alpha L} \quad (2.61)$$

therefore,

$$P \approx e^{-2\alpha L} \quad (2.62)$$

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**Figure 2.4** Wavefunction for a long barrier of finite length.

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